AEROSOLOMICS PROFILING: APPLICATION TO BIOGENIC AND ANTHROPOGENIC SAMPLES

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INTRODUCTION

Atmospheric aerosol particles consist of a complex mixture of inorganic and organic compounds. Depending on the site and the degree of pollution, organic compounds may represent up to 70% of the total dry fine particle mass in the lower troposphere, (Turpin B.J. *et al.* 2000; Saxena *et al.* 1996). Despite the significant abundance of organic compounds in aerosol particles, very little is known about their chemical composition. The number of organic compounds in aerosol particles can easily be several hundreds (Oros D.R. *et al.* 2001 a,b). These organic species are often present at trace levels (less than ng m^{-3}), and vary significantly in polarity and volatility.

In aerosolomics all the compounds present in aerosol particles are determined. Two complementary methodologies can be applied in aerosolomics. In aerosolomic fingerprinting all the detected analytes in aerosol particles are of interest, but there is no need to identify them all. In aerosolomics profiling only a small number of pre-selected analytes in aerosol particles are analysed by the methods carefully optimized for these target compounds.

Collection of nanometer size particles for both their characterization and determination is a very challenging task. Typical particle collection devices and systems, such as impactors, electrostatic precipitators, filters, particle growth in supersaturated water vapor (Simon P. *et al.* 1995) and particle into liquid, the latter being acombination of particle growth in supersaturated water and impaction in a quartz plate, are active ones in the sense that a known quantity of air needs to be drawn through the systems. Unfortunately in many cases their collection efficiency for particles significantly smaller than 100 nm is poor (Saxena *et al.* 1996, Parshintsev *et al.* 2010, Orsini *et al.* 2003).

All particle collection systems mentioned have one common limitation, namely they do not allow the particle size segregation. A differential mobility analyzer (DMA) coupled to a particle charger in whichcharged particles are size-separated in DMA is a new option. Once the particles are size-separated they can be analyzed directly by aerosol mass spectrometer (AMS), or collected on a suitable filter (Laitinen *et al.* 2010).

The chemical analysis of aerosol particles is demanding and no single technique is available for the simultaneous analysis of all organic compounds in atmospheric aerosol particles. Aerosol mass spectrometry is a good technique in the analysis of atmospheric aerosols within a short time a without sample pretreatment (Laitinen *et al.* 2009).However, it does not, unfortunately, allow the separation and determination of the individual components in the aerosol particles. In the aerosolomics profiling chromatographic techniques are needed for the individual separation and determination of the target compounds. One of the most widely used chromatographic techniques for the analysis of volatile and semi-volatile compounds in aerosol particles is gas chromatography–mass spectrometry (GC–MS) due to straightforward on-line coupling of GC with MS and the large amount of library reference spectra

available.However, highly polar and non-volatile compounds cannot be analysed without chemical derivatization by GC. Then other techniques such as high-performance liquid chromatography (HPLC), ion chromatography (IC), or capillary electrophoresis (CE) with indirect UV (PDA) detection (Khwaja *et al.* 1995, Limbeck *et al.* 1999, Soga *et al*. 1997) are beneficial..

In this work, aerosomics profiling was employed for the determination of potential marker compounds, one amine, four aldehydes, two polyols and thirteen acids in biogenic and anthropogenic aerosol samples. The results achieved were used for the development of model based on pattern recognition techniques that enable the differentiation between biogenic and anthropogenic aerosol samples and help to find real marker compounds for particle growing processes.

METHODS

Fifty nanometer and all size aerosol particles from two different sources, biogenic and anthropogenic, were studied in this research. Twelve biogenic samples, and twelve anthropogenic samples, a half containing all particle sizes and the other half containing 50 nm particles, were collected using the device described in Figure 1.
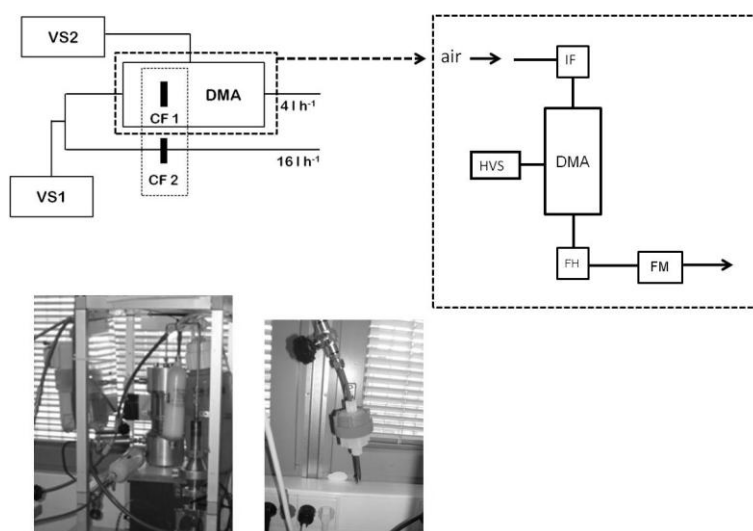

Figure 1. Dual sampling device scheme. VS, vacuum system; CF, collection filter; DMA, differential mobility analyzer; IF, ionization font; HVS, high voltage supply; FH, filter holder; FM, flow-meter

Biogenic aerosol samples were collected in spring of 2009 at the Station for Measuring Forest Ecosystem Atmosphere Relations (SMEAR II) at Hyytiälä (Finland), and anthropogenic aerosol samples were collected in summer of 2009 at the urban background station SMEAR III at Helsinki (Finland).

The method employed for the determination of the target analytes can be divided into three steps: (1) extraction of the target analytes from the filters; (2) sample preparation including derivatization, dilution, pH changes, etc; and (3), individual isolation and quantitation of the target compounds.

The extraction of the target analytes from the sampling filters and their subsequent silylation derivatization were accelerated by means of ultrasounds.

3-hydroxyglutaric, adipic, azelaic, pinoic, tartaric, vanillic, palmitic, maleic, malic, malonic, stearic, oleic and pinic acids, polyols, levoglucosan, α- D-mannose and β.-D-mannose were determined by GC-MS after derivatization. Pinoaldehyde, β-caryophyllene aldehyde., β-nocaryophyllene aldehyde and benzaldehydewere determined by LC-MS after extraction of the analytes from the filters without any additional sample preparation. Diethylamine was determined by LC-MS after a pH change of the sample using ammonium hydroxide.

The methods developed for the determination of the target compounds were validated by means of the

standard addition method using both 50 nm and all size biogenic and anthropogenic aerosol particle sample matrices. The extraction method developed was validated by comparing it with a standard reference Soxhlet extraction method.

RESULTS

The developed method was applied to twenty four samples collected from two biogenic and anthropogenic sources. A half of the samples were 50 nm particles and another half particles containing all sizes. The concentration of some analytes in all size particles was smaller than that in 50 nm particles. most probably due to the transformation of the compounds during the particle growing process or during the sampling collection affected bylong collection times, humidity, bacteria and high air flow-rate. Polyols and some aldehydes were more abundant in the anthropogenic samples, and diethylamine and vanillic acid more abundant in the biogenic samples.

There is no information in the literature about the detailed chemical composition of 50 nm particles. The data found in the literature on diethylamine in aerosol particles with a particle size range between 60 and 125 nm (Fachini *et al.* 2008) agrees with that obtained in this study.

More information is found on chemical compounds in allowing comparison to be made with our results. In general terms the result are in agreement with the data provided by the literature.

Comparison of chemical composition of in biogenic and anthropogenic aerosol particles. Statistical studies based on Principal Component Analysis (PCA) were carried out to study the differences in the chemical composition of biogenic and anthropogenic aerosol particles. There is a clear separation between the biogenic and anthropogenic samples (Figure 2). In the case of 50 nm aerosol particles, the concentration of benzaldehyde and β-D-mannose is characteristic to the samples of biogenic nature and the concentration of oleic, palmitic and stearic acid is characteristic to the anthropogenic samples. The concentration of pinoaldehyde, β-caryophyllene aldehyde, β-nocaryophyllene aldehyde and diethylamine is characteristic to the all size biogenic particles, , but the characteristic compounds are totally different in the biogenic 50 nm particle samples, opposite to the anthropogenic all size and 50 nm particle samples that contain the same characteristic compounds, namelyoleic, palmitic and stearic acids.
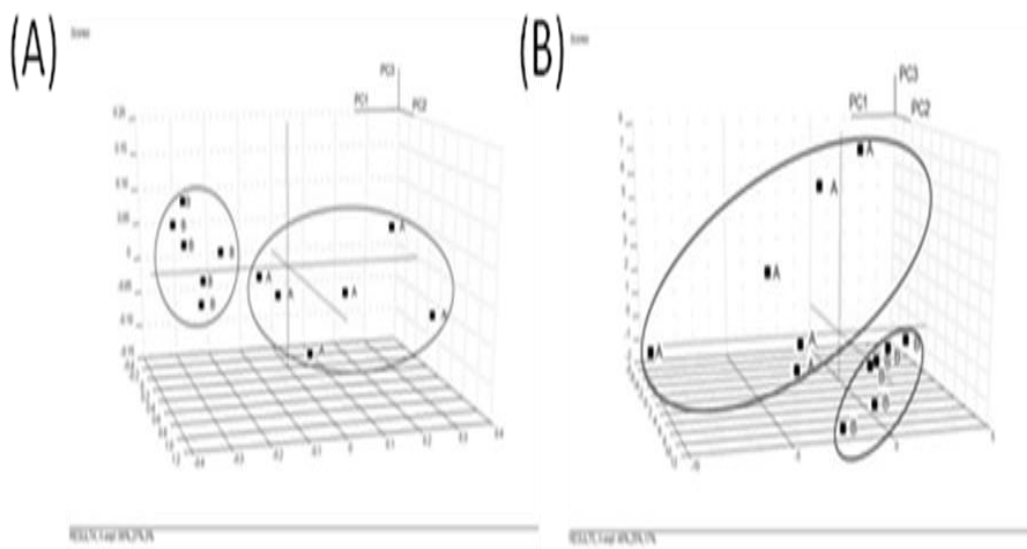

Figure 2. PCA diagrams for the comparison between biogenic and anthropogenic samples. A, 50 nm particles; B, all size particles.

Effect of the number of events on the chemical sample composition. The effect of the number of events on the particle composition was clarified using a univariate and multivariate approaches. Taking into account that sampling period is not homogeneous in the biogenic aerosol samples, a new variable, number of events per sampling period, was used as response variable in all the cases**.**

It was considered that there was correlation in those cases with a fitting between the data and model higher than 90 %. The analytes which present correlation, the type of correlation and the value obtained for the fitting are shown in Table 1.

Principal component regression (PCR) was used in order to study the relationship between the number of events per sampling period and the chemical composition of the aerosol particles in a multivariate way.

In all the biogenic and anthropogenic 50 nm and all sizes particle samples the residual validation variance was smaller than 0.5 % and R^2 of the prediction was higher than 0.9 for 2 PCs. The influence of the variables on the PCR models can be seen in Table 2. Positive and negative influence, for a target analyte, can be interpreted as a direct and inverse relationship, respectively, between the concentration of analyte and the number of events per sampling period or between the presence of the analyte and the growing process. Therefore, the information present in Table 2 can be used for the selection of marker compounds for particle growing processes.

Table 1. Influence of the target analytes on the number of events per sampling period studied by univariate models

Compound	Biogenic aerosol (50 nm)	Biogenic aerosol (all sizes)	Anthropogenic aerosol (50 nm)	Anthropogenic aerosol (all sizes)
3-Hydroxyglutaric acid	+ +			
Malic acid	+ +			
Maleic acid	+		+	
Oleic acid			–	–
Pinoic acid		+		
Pinoaldehyde	+			+
Tartaric acid	+ +			
Benzaldehyde	+ +	+ +		
β-caryophyllene aldehyde		+	+	+
β-nocaryophyllene aldehyde		+ +		+
Diethylamine				+
Levoglucosan	–			
β-D-mannose	–			
α-D-mannose	–			

+ + Positive and strong influence (R^2>0.95)
+ Positive influence (0.90>R^2>0.95)
– – Negative and strong influence (R^2>0.95)
– Negative influence (0.9>R^2>0.95)

CONCLUSIONS

The conclusions can be divided into three different parts according to the sampling and method development steps, the application of the method developed to the analysis of the aerosol particle samples, and the results obtained from the data analysis.

Several extraction and chromatographic techniques used in this study demonstrated their applicability to the analysis of selected marker compounds.

The DMA sampling enabledthe size selection for the analysis during the sampling period.

The extraction and derivatization procedures were shortened by the use of a ultrasonic probe. Twenty and thirty minutes were necessary with the method developed in comparison with 24 and 3 h necessary with the conventional method for the extraction and derivatization procedure, respectively. The replacement of ultrasonic bath with ultrasonic probe reduced the time further to the half (Medeiros *et al.* 2007, Rissanen *et al.* 2006).

The application of the method developed to biogenic and anthropogenic 50 nm and all size particle samples confirmed pinic acid oxidation process. Differences in the chemical composition of the biogenic and anthropogenic aerosol particles make possible the differentiation between biogenic and anthropogenic particles. There is correlation between the number of events per sampling period and the analyte profile. Despite the model was generated using the whole analyte profile, it was possible to clarify the influence of each individual analyte on the model. The models, once completed with additional samples, are beneficial in the selection of real marker compounds for particle growing process studies. In addition, it was possible to find correlations between the concentration of the individual marker compounds and the number of events per sampling period.

Table 2. Influence of the target analytes in the number of events per sampling period by PCR models

Compound	Biogenic aerosol (50 nm)	Biogenic aerosol (all sizes)	Anthropogenic aerosol (50 nm)	Anthropogenic aerosol (all sizes)
3-Hydroxyglutaric acid	+	+	+	+
Adipic acid	–	–	+	+ +
Azelaic acid	–	–	+	+
Palmiticacid	–	–	–	– –
Malonic acid	–	–	–	–
Malic acid	+	+	+	+
Azelaic acid	–	–		
Maleic acid	+	+	+ +	
Stearic acid	+	+	+	+
Oleic acid	–	–	– –	–
Pinoic acid		+	+	
Pinoaldehyde	+	+	+	+ +
Vainillic acid	–	–		
Tartaric acid	+	+		
Benzaldehyde	+ +	+ +	+	+
β-caryophyllene aldehyde		+ +	– –	+
β-nocaryophyllene aldehyde	–	+	– –	+
Diethylamine	–	–	+	+
Levoglucosan	–	–	+	+ +
β-D-mannose	–	– –	–	–
α-D-mannose	–	–	+	+ +

+ + Positive and strong influence

+ Positive influence

– – Negative and strong influence

– Negative influence

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